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FLOCCULANTS

FINAL REPORT

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SUBJECT:

FINAL REPORT
JUNE, 1983
COVERING WORK CARRIED OUT AT
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WITH THE ASSISTANCE OF
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ABSTRACT

A complete gel permeation chromatographic system for use with the Chromatix KMX-6 Low Angle Laser Light Scattering Photometer (LALLSP) has been assembled and extensively tested. Excellent molecular weight determinations were carried out on nonionic and anionic polyacrylamides. No satisfactory results were obtained with cationic flocculants.

The possibility of employing end-group analysis for molecular weight determination of flocculants was explored. Two analytical methods, a radiochlorine labelling and a dye partition technique, were considered, however in both cases the relative insensitivity of the method and the extensive developmental work required made them unacceptable.

Size determination of standard polystyrene beads in aqueous suspension with the Chromatix Digital Correlator accessory initially yielded poorly reproducible results. Satisfactory results were ultimately obtained, however the tempermental nature of the instrumentation made continual recalibration with known standards essential. Four different water-soluble polymers were examined, and an interesting relationship between molecular size and chemical functionalities on the polymer backbone observed.

A literature survey of polyelectrolytes and their interaction with ions in solution was carried out. The effects of polyelectrolyte-ion binding were investigated, and both physical and instrumental methods for the assessment of the extent of such binding in polymers were detailed.

The molecular weight fractionation of nonionic polyacrylamide in aqueous solution was carried out by non-solvent addition using either isopropanol or methanol, and the fractions investigated by dynamic LALLS photometry. Fractionation with isopropanol-water yielded excellent results, whereas fractionation with methanol-water produced poorly differentiated products.

The feasibility of labelling polymers with stable isotopes such as carbon-13 has been investigated. Although expensive, this may allow examination of the flocculant conformation under various conditions by spectroscopic methods. Free-radical labelling can also yield valuable information on polymer conformation.

INTRODUCTION

This report records Part II of the work performed under the contract issued by the Department of Supply and Services (DSS File No. 23SQ.23440-2-9037) on behalf of the Department of Energy, Mines, and Resources, CANMET, Coal Research Laboratories, Edmonton, Alberta. The Scientific Authority of this project was Dr. H. Hamza of the Coal Research Laboratory. Part I of this project, covering the two tasks:

1. Degradation of Polymeric Flocculants
2. Synthesis and Modification of Flocculants

was discussed in a detailed report accompanying the January summary report. The tasks covered in Part II of the contract were:

1. Determination of the Molecular Weight and Molecular Weight Distribution of Flocculants
2. Measurement of Polymer Molecular Size in Solution
3. Determination of Structure-Activity Relationships.

BACKGROUND

The production of high quality coal by coal washery techniques also yields large volumes of particulate-laden water. Synthetic organic polymeric flocculants are widely used to clarify the effluent water, thereby improving recovery of coal and yielding more environmentally acceptable waste water.

The large number of competing flocculants now available from several manufacturers has made it difficult for washery operators to determine the most satisfactory product for their application. In addition, variations in the composition of effluent water cause substantial fluctuations in the effectiveness of certain flocculants during normal operations. Determination of the chemical and physical characteristics of commercial flocculants and correlation of these characteristics with flocculant effectiveness was therefore undertaken.

The Summary Reports of earlier contracts in this series and the report of Part I of this contract detail the development of techniques for the chemical characterization of various types of commercial polymeric flocculants. This report covering the second part of the contract largely details the physical characterization of these materials.

RESULTS AND DISCUSSION

1. DETERMINATION OF FLOCCULANT MOLECULAR WEIGHT AND MOLECULAR WEIGHT DISTRIBUTION

The effectiveness of polymeric flocculants is strongly related to molecular weight (1,2), as suggested by the theory of flocculation by interparticle bridging (3). Accordingly, large numbers of molecular weight determinations have been carried out by Raylo Chemicals using various methods, as discussed in earlier Summary Reports.

1.1 Assembly and Testing of a Gel Permeation Chromatographic System

Static Low Angle Laser Light Scattering Photometry (LALLSP), found by Raylo to be the best method for molecular weight determinations, has previously yielded satisfactory results on over fifty flocculants. In addition, some molecular weight distributions were obtained by dynamic LALLSP analysis of the eluent from hand-packed gel permeation chromatographic columns. Recently, much more efficient gel permeation columns have become commercially available from Varian Ltd. (4,5). Raylo Chemicals was asked to assemble and test a complete aqueous gel permeation chromatographic system based on these columns for the Coal Research Laboratory. This was assembled at the Clover Bar site of Coal Research Laboratory and tested extensively.

The system consists of an Applied Chromatographic Systems pump, a Rheodyne 7126 loop injector valve, Varian TSK-Gel 5000 PW and 6000 PW gel permeation chromatographic columns, the Chromatix KMX-6 LALLS

Photometer, and a Waters R-401 Differential Refractometer (see Diagram 1). The KMX-6 and R-401 are connected to an LDS-2 microcomputer system, which carries out the extensive calculations required.

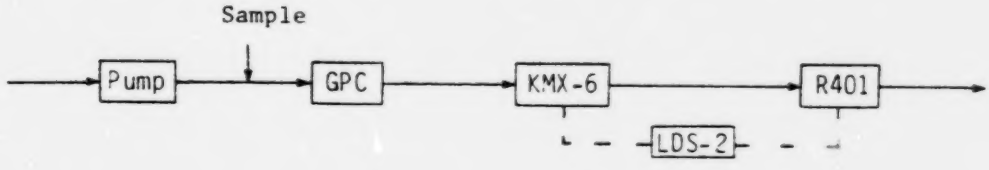

Diagram 1. Layout of gel permeation chromatographic system.

Dynamic Light Scattering Analyses

Varian 6000 PW Column:

Over 200 dynamic light scattering analyses of a large number of polymeric standards and flocculants have been carried out. The results indicated that the Varian 6000 PW Column could satisfactorily analyse nonionic and anionic polyacrylamides of over 500,000 daltons, as noted in Table 1. Some erratic results obtained in dynamic LALLS analyses using the Varian 6000 PW Column were attributable to either start-up problems in the operating system or use of insufficient weight of sample. Thus after repeated tests with polyacrylamides of various molecular weights, the minimum sample weight for reproducible results was found to be:

$$\text{weight (g)} = 500/\text{molecular weight}$$

Alternatively, if a standard 100 microliter injection loop is used, the minimum polymer concentration should be:

$$\text{concentration (g/ml)} = 5000/\text{molecular weight}$$

As long as the viscosity of the polymer solution does not cause problems, higher concentrations are acceptable.

The reproducibility of results from this column was tested by repeated analyses of the PolySciences polyacrylamide standard PS 2806. The mean weight average molecular weight over sixteen runs was 6.36 million daltons, with a standard deviation of 0.89 million. This compares favourably with a similar series of six analyses run on hand-packed columns at Raylo Chemicals discussed in the previous Summary Report. An average molecular weight of 7.21 million daltons was found, with a standard deviation of 1.17 million.

Flocculant sample 4, a nonionic polyacrylamide, was analyzed in triplicate and an average molecular weight of 7.02 million daltons with a standard deviation of 1.32 million observed. This compares well with a series of six analyses carried out on hand-packed columns in the previous phase of the contract in which an average molecular weight of 7.32 million daltons with a standard deviation of 0.77 million was observed.

These highly reproducible results led us to consider analysis of of ionic flocculants. Accordingly flocculant sample 39, an anionic polyacrylamide, was analyzed by dynamic LALLS photometry and found to

have an average molecular weight of 6.82 million daltons and a standard deviation of 0.43 million. This compares with a molecular weight of 6.2 million daltons determined by static LALLS photometry.

Analysis of cationic polyacrylamides and polyamines on the Varian 6000 PW column was attempted, however all of the polymer was absorbed by the column in both cases. Further study of cationic polymers was halted lest a buildup of bound material degrade the quality of the column. A similar adsorption has been reversed by heating the Varian columns (6), however lack of time and suitable equipment for column heating prevented experimentation with this technique.

Overall, the Varian 6000 PW column performed admirably for the analysis of nonionic and anionic polyacrylamides. Reproducibility of analytical results equalled that of hand-packed porous glass columns, previously the best available (7), whereas the analysis time was a fifth of that required on a comparable porous glass column analytical system. This column, therefore, represents the best analytical technology available for high molecular weight water soluble nonionic and anionic polymers.

Varian 5000 PW Column:

The Varian 5000 PW column was also tested with a variety of polymer standards as noted in Table 2. Polyacrylamide standards with molecular weights of 5 million, 1 million and 500 thousand daltons were largely excluded from the column. This column therefore is unsuitable

for polyacrylamide-based flocculants, all of which exceeded 1 million daltons. However, the Varian 5000 PW column was appropriate for polyacrylamide standards below 500,000, with an estimated lower limit of 80,000. A shortage of low molecular weight standards precluded extensive testing below this molecular weight.

In addition, polyamine flocculant samples 9 and 56 were successfully analyzed using the 5000 PW column, although they consistently yielded molecular weights far higher than static LALLS analyses run previously. Thus sample 9, previously determined to have a molecular weight of 85,000 daltons, was found to have a molecular weight of 299,000 in repeated runs. Sample 56 was previously found to have a molecular weight of 336,000 daltons by static LALLS photometry, whereas a molecular weight of 585,000 was found using the recently assembled dynamic LALLS system.

A series of polyethylene oxide molecular weight standards were therefore analyzed by dynamic LALLS Photometry employing the 5000 PW column. The results, noted in Table 2, are consistently far too high and often poorly reproducible. Similar results were obtained for polyacrylamide suggesting the column may be flawed. Repeated tests with other well characterized standards should be carried out.

The gel permeation chromatographic system is therefore operating satisfactorily in spite of difficulties with one of the columns. The microcomputer has allowed all data from successful analyses to be

stored on computer disk, easily accessible for reassessment in the future.

1.2 Molecular Weight Determination by End-Group Analysis

End-group analysis has been widely used to determine the number average molecular weights of polymers (8,9,10). Its application has usually been limited to polymers with molecular weights of 50,000 or below. This is far below the range of our interest for both polyamine and polyacrylamide-based flocculants. A brief literature search was conducted for methods applicable to either type of polymer.

Two methods which might be adapted for analysis of polyacrylamide-based polymers were found. The first, based on the radiochemical determination of the degree of unsaturation of the polymer in question (11), involves treatment of the polymer with radiochlorine and measurement of the absorbed activity. As polyacrylamide polymerization terminates through disproportionation (12), a single site of unsaturation should be present for every two polyacrylamide macromolecules, as illustrated below.

This analytical procedure successfully detected unsaturation at a level

of 0.01 mole %, corresponding to a single site of unsaturation in a polyacrylamide with a molecular weight of 700,000 daltons. This procedure was however developed using polyisobutene, and would not be directly applicable to polymers soluble only in water. As extensive developmental work would be needed to modify this method, and its sensitivity appears to be too low for useful analysis of the polyacrylamides under investigation, this method should not be considered for further study.

A dye partition technique has recently been used to investigate the sulphate content of organic-soluble polymers prepared by free-radical polymerization (13,14). The polystyrene, poly (methyl methacrylate), and poly (vinyl acetate) were all prepared using potassium persulphate initiator. An average of two sulphate end-groups per polymer chain up to molecular weights of one million could be detected with this technique. This method is therefore one of the most sensitive available for end-group analysis. Some developmental work would, however, be needed to cleanly convert the polyacrylamide-based flocculants under study to organic-soluble analogues. Furthermore, the end-group determination procedure is sensitive only to strong acid end-groups such as sulphate derived from persulphate polymerization initiators. Thus polymerization by irradiation would yield products that gave no reaction to this test.

Both methods discussed here would require developmental work

before they could be applied to polyacrylamide-based flocculants. In addition, the radiochlorine method would require expensive equipment. On the other hand, the dye partition technique could be carried out easily in any laboratory. Neither technique appears sufficiently sensitive to accurately determine polymer molecular weights, however the dye partition technique may be useful in determining the method of polymerization.

2. MEASUREMENT OF POLYMER MOLECULAR SIZE IN SOLUTION

The performance of polymeric flocculants is affected by the identity and concentration of inorganic ions in solution (15). As both of these variables affect the molecular size of polyelectrolytes in solution (16), an experimental study and a literature survey were both planned in consultation with the Scientific Authority, Dr. Hamza.

2.1 Size Determination with the Chromatix Digital Correlator

Quasielastic light scattering (QLS), a relatively new technique for particle sizing, has been used extensively in recent polymer analyses (17,18,19,20). Raylo Chemicals therefore purchased a Chromatix Digital Correlator accessory for the KMX-6 LALLS Photometer in the previous stage of this contract.

Tests of the Digital Correlator were carried out with polystyrene latex bead standards in aqueous suspension. The aqueous suspension of, typically, 100 nm diameter latex spheres was pumped slowly through an 800 nm filter and into the KMX-6 LALLS Photometer cell. Analysis of

scattered light by light-beating or autocorrelation techniques allowed the determination of the translational diffusion coefficient D_T. The molecular size was then calculated using the Stokes-Einstein equation:

$$\text{radius} = kT/6\pi\eta D_T$$

where k is Boltzmann's constant, T is temperature, and η is solvent viscosity.

Typically, a single size analysis used the averaged results of 5 individual runs, and took less than 10 minutes to complete. The limits to the application of this technique were the extensive time required to prepare the samples, and the time required to ascertain the reliability and significance of the results.

Over 200 analyses were carried out, the majority of latex beads of sizes comparable to high molecular weight polyacrylamides in solution. Results of the analyses were extremely sensitive to cell positioning in the KMX-6 Photometer. Thus reliable analyses using this technique of polystyrene beads with a nominal diameter of 100 nm yielded an average diameter of 89.4 nm, yet sequential runs yielded diameters of 82.8 nm, 46.5 nm, and 87.2 nm after apparently minor changes in cell positioning. This sensitivity indicates calibration of the system with known standards should be done before and after each series of polymer analyses.

A selection of cationic polyamine and nonionic polyacrylamide polymers in 0.1 molar sodium sulphate solution was investigated by

quasielastic light scattering. The cationic and nonionic samples were found to have molecular diameters that increased in relation to their molecular weights, albeit irregularly (see Table 3). The ratio of volume to molecular mass, shown in normalized form in Table 4, shows great variations which may depend on the chemical structure of the polymer in question. Thus sample 57, a polydiallyldimethylammonium chloride, has one hydrophilic quaternary ammonium group per backbone monomer unit of 126 daltons (see Table 4). This polymer therefore has both the lowest content of hydrophilic functionalities and the least extended molecular conformation of the four polymers successfully tested. Sample 16, a poly (2-hydroxypropyl-1-N-dimethyl ammonium chloride) has two hydrophilic groups, a quaternary ammonium and a hydroxyl functionality per monomer backbone unit of 112 daltons. This polymer has both the greatest content of hydrophilic groups and the most extended molecular chain in solution. The other two polymers have intermediate values of both variables. In these polymers, a substantially higher content of hydrophilic groups indicates a more extended molecular conformation.

A correlation between molecular size and content of hydrophilic groups in different types of polymers has been found. These observations must now be confirmed and expanded to include other types of polymeric flocculants.

2.2 Literature Survey of Polyelectrolytes in Solution

Great advances have recently been made in both the theoretical and experimental investigation of the size of charged polymers or polyelectrolytes in solution. Raylo was therefore requested to carry out a literature survey in this area, with particular reference to the effects of various counterions on the polyelectrolyte, and new analytical methods used in this field.

A polyelectrolyte in solution can be considered an extremely long rod or random coil with a reasonably constant charge per unit length. Surrounding this are a large number of counterions at varying distances from the polymer chain. The distance and mode of interaction between the polyelectrolyte and its counterions have a great influence on the conformation of the macromolecule in solution. This in turn modifies the size, flocculating ability, and solubility of the polymer.

Four Regions Within A Polyelectrolyte Solution

Consider for example a polyacrylate ion in solution in the presence of various counterions. If sufficient protons are present to neutralize the charge, then each carboxylate group, shown as (-) in Diagram 2, would covalently bind one proton, shown as (+). The resulting polymer, polyacrylic acid, would adopt a random coil configuration essentially undisturbed by additional ionic content.

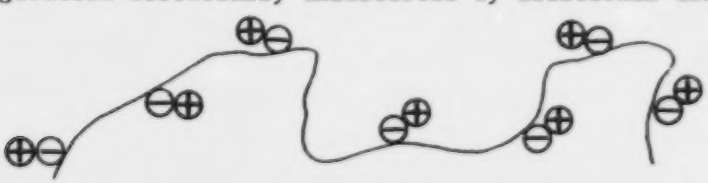

Diagram 2: Anionic polyelectrolyte with tightly bound counterion.

A counterion such as sodium, on the contrary, would tend to be distributed throughout the solution, with a somewhat greater proportion of the total ion content close to the ionic backbone of the polymer as a result of electrostatic forces. For a polyelectrolyte in a random coil configuration, the total solution volume can be divided into four regions (21,22). The most closely bound ions are termed site-bound, as they are held in contact with a specific site on the backbone (region 1 in Diagram 3).

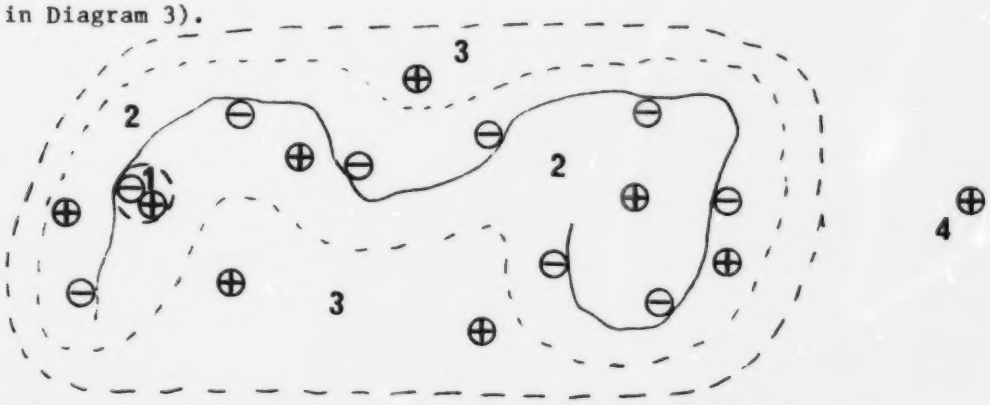

Diagram 3. Four regions around an anionic polyelectrolyte.

Secondly, counterions electrostatically bound to the polymer backbone but free to move within the cylindrical potential well are termed territorially (21) or atmospherically (23) bound (region 2 in Diagram 3). More counterions will remain within the spherical volume occupied by the polyelectrolyte, however these are mobile and

continually diffusing throughout the solution (region 3 in Diagram 3). Finally, some counterions are normally present in the solution between the individual macromolecules (region 4 in Diagram 3).

Region 1

The distribution of counterions between these four regions will greatly influence the conformation and size of the polyelectrolyte. Thus counterions that are in region 1, that is, intimate physical contact with an ionic site on the backbone, will effectively act as a nonionic moiety. Such contact would cause loss of water from the inner solution sphere around the counterion. The extreme was discussed earlier, in which protons bound covalently to all anionic sites on a polyacrylate backbone to produce a nonionic polymer.

Region 2

The counterions in region 2 strongly interact with the polyelectrolyte as well, resulting in substantial perturbations in their outer ion hydration layers. These perturbations can be investigated by volumetric measurements (24,25) or analysis of variations in the index of refraction (26). In addition, nuclear magnetic resonance spectroscopy of such diverse nuclei as magnesium-25 (27), sodium-23 (28,29), lithium-7 (30) and rubidium-87 (31) has been used to determine the extent of binding of these ions. This region, calculated to extend out to a distance of between 0.6 nm (22) and 1.4 nm (28) from the polyelectrolyte chain, has a high ionic concentration.

Region 3

Region 3 includes the region comparatively distant from the polyelectrolyte chain, yet within the volume occupied by its random coil. The hydration spheres of counterions within this region are unperturbed and the ions are usually considered to be free (21). However, this region has a higher ionic concentration than region 4, the volume outside all macromolecular random coils. Therefore osmotic forces will attempt to increase the volume of region 3, enlarging the size of the macromolecule.

Region 4

Region 4, the interstitial solvent, contains the lowest concentration of counterions. This region is usually absent in typical flocculants at normal operating concentrations, as will be explained below.

Relative Volumes of the Four Regions

The volumes occupied by each of the four regions discussed above is very important in considering the effects of different counterions on a polyelectrolyte.

The volume of region 1 is essentially negligible as a proportion of the total solution. Region 2, on the other hand, has been estimated to extend between 0.6 nm (22) and 1.4 nm (28) from the polyelectrolyte backbone. Thus the volume of region 2 of a typical anionic

polyacrylamide solution with a concentration of 0.1% would occupy between 0.6% and 2.3% of the total volume of the solution, as shown in Appendix 1. If this polymer has a molecular weight of about 7 million, the typical molecular diameter of a somewhat extended random coil would be 200 nm or more (32). In this case the region of territorial binding would only make up between 1.5 and 6.5% of the total volume occupied by the macromolecule random coil, depending on the thickness of the shell corresponding to region 2 about the polyelectrolyte chain. The volume of this region is therefore far smaller than the volumes of regions 3 and 4.

The volume of region 3, that occupied by the random coil of the polyelectrolyte, depends largely on the extension of the polyelectrolyte chain. Thus a nonionic polyacrylamide with a molecular weight of 7 million has a molecular diameter of 100 nm in aqueous solution (32,33). Polyacrylamides with increasing degrees of hydrolysis have been found by Raylo to exhibit viscosities of between 8 and 50 times that of the corresponding neutral polymer. As solution viscosity is proportional to the molecular size (34), the diameter of the random coil must be twice and 3.6 times that of the nonionic polymer, or 200 nm and 360 nm respectively. The volume occupied by the random coils can be shown to occupy from one third to all of the available volume of solution in salt-free systems.

Region 4 as obtained by difference could make up to 70% of a

polyelectrolyte solution volume for polyacrylamides with a low degree of ionic functionalization, however in most cases, no free volume exists between the extended macromolecules. Addition of inorganic salt will cause collapse of the polyelectrolyte coil to its relaxed configuration, reducing its volume fraction to about 4% of the total solution volume.

Counterion-Polyelectrolyte Binding

G.S. Manning has developed an extremely useful empirical theory for analysis of counterion-polyelectrolyte binding (21). He proposes that all counterions can be sharply divided into the bound (regions 1 and 2) and the unbound (regions 3 and 4). Further, if f is the charge fraction of the polyion which is uncompensated by bound counterions, then:

$$f = 1/N\xi \quad \text{if} \quad \xi > N^{-1}$$

$$f = 1 \quad \text{if} \quad \xi < N^{-1}$$

where N is the counterion valence and

$$\xi = q^2/EKTb$$

where q is the protonic charge, E the bulk dielectric constant of the solvent, K Boltzmann's Constant, T the temperature (Kelvin), and b the spacing of charges along the polyelectrolyte backbone. For sodium polyacrylate,

$$\xi = 2.85$$

This value, a measure of linear polyion charge density, will

decrease for partially hydrolyzed polyacrylamide in proportion to the relative number of acrylate groups remaining. Thus for sodium polyacrylate:

$$f = 1/(1 \times 2.85) = 0.35$$

Therefore 35% of the carboxylate groups are unbound, and conversely, 65% of the polyelectrolyte's anionic charge is neutralized by sodium counterions in regions 1 and 2.

For polyacrylamide with a 35% degree of hydrolysis, the value of the linear polyion charge density is:

$$\xi = 2.85 \times 0.35 = 1.0$$

and for the sodium salt of this polymer:

$$f = 1/(1 \times 1.0) = 1$$

Thus no sodium ion should theoretically be retained in region 2. If the calcium salt of this polymer is considered, where the value of N is 2, then:

$$f = 1/(2 \times 1.0) = 0.5$$

Half of the polyelectrolyte charge would therefore be neutralized by calcium in regions 1 and 2. Note that this means divalent counterions will successfully compete with monovalent counterions.

A very elegant demonstration of the preferential binding of counterions of higher charge was recently carried out (35). A solution of sodium chondroitin ($\xi = 1.15$), a polysaccharide polyelectrolyte, was prepared, and a small amount of strontium added. The divalent

strontium displaced an equivalent amount of bound sodium. Trivalent lanthanum was then incrementally added, and the distribution of ions noted.

For this polyelectrolyte, the value of the uncompensated charge fraction f for mono-, di-, and trivalent ions can be calculated to be 0.87, 0.44, and 0.29 respectively as shown below:

$$f = 1/(N \times 1.15)$$

This could be restated as follows; 13% of the polyelectrolyte charge will be matched by bound ions if only monovalent counterions are present. This figure will rise to 56% and 71% if sufficient di- and trivalent counterions are available.

Addition of trivalent lanthanum therefore displaced bound monovalent sodium until about 13% of the polyion charge was neutralized by lanthanum. At that point, all sodium had been displaced, and the trace of divalent strontium remained bound. Further increments of lanthanum were immediately bound by the polyion without any other change to the system until 56% of the polyion charge was accounted for by the trivalent counterion. At this point, the strontium ion was totally displaced by the lanthanum. More lanthanum then continued to bind with the polyelectrolyte until approximately 70% polyion charge neutralization had occurred.

The above experiment was carried out with a polyelectrolyte and counterions that exhibit only ionic interactions. While this may be a

satisfactory analogy for cationic flocculants, anionic flocculants contain carboxylate groups, which can interact specifically with certain cations such as protons or copper (II) to produce site-binding. If, however, no evidence of significant site binding can be found, then the counterion with the greatest charge will preferentially bind with the polyelectrolyte.

This suggests a simple experimental technique to determine if a counterion is irreversibly site-bound. Addition of a cationic polyelectrolyte such as polydiallyldimethylammonium chloride would normally bind efficiently to an anionic polyelectrolyte, competing successfully with any solvated cations in region 2. Cations that were tightly site-bound in region 1 would remain, reducing the titre of polycation required for the colorimetric (36) or conductometric (37) endpoint.

Another technique used to assess the extent of site-binding specifically in the case of manganese is electron spin resonance (23,38). Changes in the hyperfine splitting of the esr spectrum of the manganese ion are believed to be attributable to the displacement of water of solution by the anionic group of polysulphonate or polyacrylate. This technique was used in conjunction with nuclear magnetic resonance studies to assess cation residence in regions 1 and 2.

Manning's explanation of counterion-polyelectrolyte binding has

been verified satisfactorily by a large number of workers (35,39,40,41, 42,43,44,45,46), although certain authors have pointed out theoretical shortcomings in his analysis (28,29,30,47,48). Application of his findings to the study of flocculation must involve confirmation that his theory works for polyelectrolytes with low ionic content and investigation of the extent of site-binding of ions found in coal washery effluent waters.

Analytical Methods

Small-angle neutron scattering (SANS) is a relatively new technique for the analysis of polymers (49). This technique yields the molecular dimensions and persistence length of polymers. This is similar to results obtainable with the Chromatix Digital Correlator accessory for the KMX-6 for polymers in solution. SANS can also be applied to solids and gels (50). This method has been successfully applied to the determination of an ordered arrangement of polymethacrylate molecules in solution (51) and analysis of lithium dodecyl sulphate micelle structure (52). It therefore should reveal changes in inter- and intra- molecular interactions after changes in ionic content. A unique advantage is the ability to specifically investigate a deuterated polymer in the presence of non-deuterated polymer. Application of this comparatively recent technique will require substantial background work.

Determination of the electrical mobility of macromolecules by

quasielastic laser light scattering has been used to determine ionic binding (35). This technique would require generation of an external electrical field about the KMX-6 photometer cell. The extent of binding of various counterions to any fully soluble polymer under a wide variety of conditions could be investigated. Of course, in the absence of an external electrical field, the analysis reverts to the size determination of the macromolecule under varying conditions.

Quasielastic light scattering has been used specifically for the study of partially hydrolyzed polyacrylamides (41). The scattering angle employed by these workers was varied between 30 and 90 degrees. The available scattering angles of the KMX-6, either less than 7 degrees or more than 173 degrees, may be too restrictive. The possibility of modifying the KMX-6 should be investigated.

3. DETERMINATION OF STRUCTURE-ACTIVITY RELATIONSHIPS

The object of this project was to chemically and physically characterize commercial polymeric flocculants so that the Coal Research Laboratory could correlate these characteristics with their flocculating properties. This would ultimately provide criteria for the preparation of superior flocculants for specific applications. The results of these characterization studies and samples of various polymers prepared by Raylo in the course of this contract have been delivered to the Coal Research Laboratory for assessment at some future date.

3.1 Fractionation of Polymers

The relationship between flocculating ability and high molecular weight has been repeatedly stressed. The Summary Report of the previous contract in this series discussed fractionation of a nonionic polyacrylamide flocculant to provide samples of varying molecular weight. These were used to assess the importance of molecular weight in flocculation of coal fines. A similar fractionation procedure using addition of the non-solvent methanol to an aqueous polymer solution was attempted with other flocculants, but failed. Development of a reproducible fractionation technique was therefore investigated.

A 0.5% solution of PolySciences nonionic polyacrylamide standard PS2806 was fractionated using incremental addition of either methanol or isopropanol non-solvents, and the resulting fractions analyzed by dynamic LALLS photometry. The fractions isolated during the procedure using isopropanol addition showed the expected changes in molecular weight, as noted in Table 5. Those prepared with methanol non-solvent addition, on the other hand, showed little variation in molecular weight over the various fractions as noted in Table 6, indicating that no real fractionation had occurred. It should be noted that the results of analyses of the fractions prepared with isopropanol have been corrected, as several known standards yielded exceptionally low molecular weight analyses at this time.

The success of isopropanol fractionation suggested that it should become a standard procedure for polyacrylamide flocculants. The application of this technique to anionic and cationic polyacrylamide-based flocculants should be possible.

3.2 Polymer Labelling

Discussions with the Scientific Authority revealed the need to investigate flocculant conformation before, during and after flocculation occurs. As flocculants are normally employed in concentrations below 0.05%, most of the techniques discussed in the polyelectrolyte literature survey are impractical. However suitable enrichment or labelling should allow certain sensitive spectroscopic methods to be employed.

Isotopic Enrichment

Carbon-13 magnetic resonance spectroscopy has been used extensively for study of polymer conformation and configuration (53, 54). However carbon-13 magnetic resonance spectra obtained by Raylo Chemicals in previous stages of the contract required flocculant concentrations in excess of 1% for reasonable analysis times. To obtain spectra at typical flocculant usage levels (0.05%), a twenty-fold enrichment of carbon-13 must be carried out. As carbon-13 makes up 1.1% of natural carbon, a polymer containing 20% carbon-13 at a specific location would be required.

No commercial sources of such a polymer exist. Syntheses of small

amounts of certain flocculants using procedures previously employed by Raylo Chemicals were reviewed, and approximate costs estimated. Thus preparation of a few grams of carbon-13 enriched poly(2-hydroxypropyl-1-N-dimethylammonium sulphate) should cost approximately $3,000 plus the cost of enriched monomer. As no enriched acrylamide is commercially available, these monomers must be first synthesized, so the price of enriched nonionic polyacrylamide would be approximately $6,000 plus the cost of enriched carbon dioxide. A formal quotation for the custom synthesis of any desired polymer will be made if this proposal is to be pursued.

Spin Labelling of Polymers

The molecular motion of macromolecules in solution has been studied by attaching spin labels and obtaining the electron spin resonance (e.s.r.) spectrum of the polymer (55). The e.s.r. spectrum line shape changes considerably as the mobility and tumbling rate of a free-radical changes. Thus the spectrum of a spin label attached to a polymer can be very different from that of the same label attached to a low molecular weight oligomer. Adsorbtion of the polymer onto a solid would also cause similar changes. The solution characteristics of both polyacrylamide-based (56), and polyacrylic acid-based (57) polymers have been investigated by this technique. This technique has also been used to elucidate the mechanism and extent of both poly(vinyl acetate) and polystyrene binding to alumina, titanium dioxide, glass and silica (58). Application of this extremely sensitive technique to flocculation by polyacrylamide and other polymers could be extremely

informative.

Such an analysis would first require incorporation of, typically, 1% of a nitroxide-containing spin label to the polyacrylamide or polyamine flocculant. The e.s.r. spectrum both of the flocculant in solution before particulate addition and of the flocculated solid would then be compared.

CONCLUSIONS

The gel permeation chromatographic system designed to operate in conjunction with the Chromatix KMX-6 LALLS Photometer for polymer molecular determinations has been installed. One of two commercial columns, a Varian 6000 PW column, gave excellent molecular weight determinations of high molecular weight anionic and nonionic polyacrylamides, the most common type of commercial flocculant. These results, although comparable to those obtained by Raylo with hand-packed porous glass columns, were obtained in far less time. The Varian 5000 PW column, on the other hand, yielded poorly reproducible and consistently high results with both standards and previously tested flocculants.

Molecular weight determination by end-group analysis was the subject of a brief literature search, however no techniques suitable for high molecular weight polymers were found.

The use of the Chromatix Digital Correlator accessory to the KMX-6 LALLS Photometer for the size determination of polystyrene latex bead standards and certain polymeric flocculants was ultimately successful. A correlation between the density of hydrophilic groups on the polymer and the expansion of the macromolecule in solution was observed.

A literature survey of polyelectrolyte-ion interactions suggested several new analytical methods to investigate this phenomenon. Nuclear magnetic resonance and electron spin resonance spectroscopy represent simple yet revealing techniques with great potential in this field.

Molecular weight fractionation of a nonionic polyacrylamide using isopropanol as a non-solvent was successfully carried out. This technique appears to be applicable to other polyacrylamide-based flocculants.

Polymer labelling with stable isotopes or spin-labels has great potential for allowing spectroscopic analysis of the process of flocculation. As no commercial polymers are presently available, a substantial synthetic program would be required.

RECOMMENDATIONS

Gel permeation chromatographic analyses of high molecular weight nonionic and anionic flocculants can begin at once. The purchase of smaller pore size columns in the Varian PW series may correct the difficulties with the 5000 PW column.

The Chromatix Digital Correlator accessory acted extremely temperamentally, however a sustained effort should yield results of great value. A long term experimental program should be commenced whenever appropriate. The possibility of obtaining a cell that has a wider scattering angle should be investigated.

The literature survey of polyelectrolytes revealed many interesting analytical techniques of value for determining the effects of polyelectrolyte-ion interactions. The excellent nuclear magnetic resonance spectral facilities at the University of Alberta make this particular technique an excellent candidate for immediate use.

Determination of more structure-activity relationships in flocculation would be assisted by spectroscopic investigation of labelled polymers. A synthetic program for the preparation of a series of suitable candidates should be commenced.

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APPENDIX

VOLUME OF REGION 2, THE REGION OF TERRITORIAL BINDING IN POLYELECTROLYTES

The calculations assume that the polymer has a molecular weight of about 7 million and a chain radius of 0.4 nm - typical for a polyacrylamide. The territorial region was assumed to extend from between 0.6 to 1.4 nm from the polymer chain, as shown in Diagram 4:

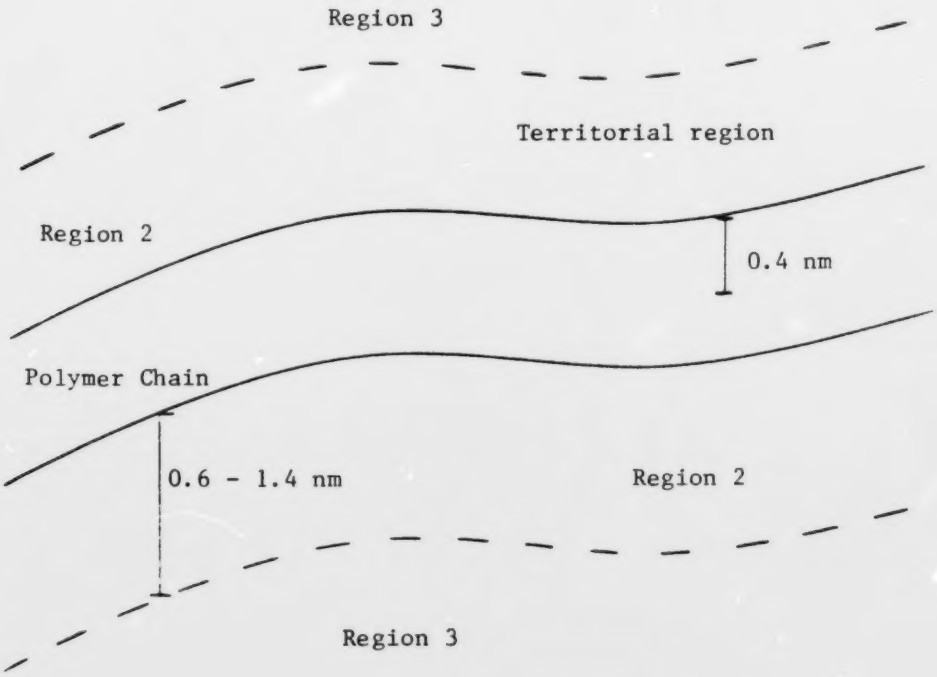

Diagram 4: Polyelectrolyte and surrounding regions.

The weight of one macromolecule is:

$$\frac{7 \times 10^{6} \text{ g/mole}}{6.02 \times 10^{23} \text{ molecule/mole}} = 1.15 \times 10^{-17} \text{ g/molecule}$$

Assuming a density of 1 for the polymer, each molecule would therefore occupy:

$$\text{Volume} = 1.15 \times 10^{-17} \text{ cm}^3 = 1.15 \times 10^{4} \text{ nm}^3$$

in the solid state. Therefore, in a 0.1% solution as is commonly prepared, each molecule has available

$$1.15 \times 10^{4} \text{ nm}^3 \times 10^{3} = 1.15 \times 10^{7} \text{ nm}^3$$

The volume occupied may be less than that available depending on the size of the random coil.

The volume of the region of territorial binding can be considered the volume of a cylindrical shell from 0.6 to 1.4 nm thick about the polymer backbone of radius 0.4 nm extending the full length of the polymer molecule. A polyacrylamide of molecular weight 7 million is composed of about 100,000 monomer units, each 0.25 nm in length. Its total length is therefore 2.5×10^{4} nm. The minimum volume in the

region of territorial binding with a shell thickness of 0.6 nm is:

$$\text{Volume} = \text{length} \times (\text{cylinder area} - \text{backbone area})$$

$$= 2.5 \times 10^4 \times \pi \times ((0.4 + 0.6)^2 - 0.4^2)\ \text{nm}^3$$

$$= 2.5 \times 10^4 \times 2.64\ \text{nm}^3$$

$$= 6.70 \times 10^4\ \text{nm}^3$$

The maximum volume of the territorial binding region, assuming a shell thickness of 1.4 nm, is:

$$\text{Volume} = 2.5 \times 10^4 \times \pi \times ((0.4 + 1.4)^2 - 0.4^2)\ \text{nm}^3$$

$$= 2.5 \times 10^4 \times 10.4$$

$$= 2.58 \times 10^5\ \text{nm}^3$$

The proportion of the solution volume occupied by the region of territorial binding can be calculated by dividing the minimum and maximum by the total volume available.

$$\text{Minimum proportion} = 6.70 \times 10^4 / 1.15 \times 10^7$$

$$= 5.8 \times 10^{-3}$$

$$= 0.58\%$$

$$\text{Maximum proportion} = 2.58 \times 10^5 / 1.15 \times 10^7$$

$$= 2.33 \times 10^{-2}$$

$$= 2.33\%$$

TABLE 1

Dynamic LALLS analyses of certain nonionic and anionic polyacrylamides using a Varian 6000 PW column.

Sample	Molecular Weight (millions)	Standard Deviation (millions)	Previous Results* (millions)
PS 2806	6.36	0.89	7.21
4	7.02	1.32	7.32
39	6.82	0.43	6.20
1M	2.23	0.53	2.17

* Dynamic analyses using porous glass columns hand-packed by Raylo.

TABLE 2

Dynamic LALLS photometry of certain standards and flocculants using a Varian 5000 PW column.

Sample	Molecular Weight (thousands)	Standard Deviation (thousands)	Previous Value (thousands)
9	299	9	85
56	585	—	336
PAM-500,000	2850	1300	--
PAM-100,000	822	128	--
PEO-594,000	2690	60	--
PEO-252,000	934	325	--
PEO-145,000	630	323	--
PEO-86,000	277	85	--

PAM - Polyacrylamide standard

PEO - Polyethylene oxide standard

TABLE 3

Molecular diameters of polymers in solution as determined by the Chromatix Digital Correlator.

Sample	Diameter (nm)	MW (thousands)
57	5.9	74
16	37.2	350
PS 2806	49.5	6360
96	66.9	15200

TABLE 4

Comparison of polymer molecular volume and hydrophilic functionality content.

Sample	Molecular Volume/g (normalized)	Molecular Mass Hydrophilic Group	Hydrophilic Groups/g (normalized)
57	0.15	126	0.18
16	7.7	56	2.04
PS 2806	1.0	71	1.0
96	1.03	73	0.92

TABLE 5

Molecular weights of fractions of PS 2806 prepared using isopropanol as non-solvent.

Sample	Weight (g)	Molecular Weight* (millions)
PS 2806	2.50	6.36
Fraction 1	0.31	6.66
Fraction 2	1.39	8.52
Fraction 3	0.23	6.21
Fraction 4	0.19	4.18
Fraction 5	0.35	2.19

* Values of all fractions corrected for systematic error.

TABLE 6

Molecular weights of fractions of PS 2806 prepared using methanol as non-solvent.

Sample	Weight (g)	Molecular Weight (millions)
PS 2806	2.5	6.36
Fraction 1	0.54	4.03
Fraction 2	0.49	4.32
Fraction 3	0.26	4.35
Fraction 4	0.12	4.81
Fraction 5	0.08	4.26
Fraction 6	0.01	5.36
Fraction 7	0.82	3.18
Fraction 8	0.21	4.08